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PAPERMAKING ADDITIVE
[Seishiyo tenkazai]

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1. Title of the Invention

PAPERMAKING ADDITIVE

2. Claim(s)

1) A papermaking additive characterized by polymerizing a vinyl-based monomer composed essentially of a (meth)acrylamide monomer in the presence of a water-soluble polymer.

2) The composition of Claim 1 wherein the water-soluble polymer is composed essentially of a reactive vinyl monomer and is a copolymer comprising one or more of the monomers (A) to (D) shown below.

(A) (Meth)acrylamide monomer

(B) Anionic vinyl monomer

(C) Cationic vinyl monomer

(D) Nonionic vinyl monomer

3) The composition of Claim (1) wherein the vinyl-based monomer polymerized in the presence of a water-soluble polymer is copolymerized with a homopolymer of a (meth)acrylamide, a (meth)acrylamide monomer, and further, a monomer selected from one or more monomers (E) to (G) shown below.

(E) Anionic vinyl monomer

(F) Cationic vinyl monomer

(G) Nonionic vinyl monomer

4) The composition of Claim (1) wherein the solid content, based on the water-soluble polymer, is 3 to 60 wt.% of the total solid content

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based on the final product obtained by polymerizing the vinyl-based monomer composed essentially of a (meth)acrylamide monomer in the presence thereof.

5) The composition of Claim 2 wherein the reactive vinyl monomer constituent is 0.01 to 20 mol.% in the water-soluble polymer.

6) A paper characterized by adding a range of 0.03 to 3 wt.% of the papermaking additive of Claim 1 with respect to the solid content of a pulp raw material for papermaking.

7) A method for manufacturing paper characterized by adding a range of 0.03 to 3 wt.% of the papermaking additive of Claim 1 with respect to the solid content of a pulp raw material for papermaking.

3. Detailed Specifications

(Field of Industrial Application)

/608

The present invention relates to a paper strengthening agent, and in further detail, a paper strengthening agent wherein the variation in the effect with respect to the pH variation of a pulp slurry during papermaking (referred to as "papermaking pH," hereafter) is small, and moreover, the reduction in the effect with respect to the dissolved constituents, e.g., inorganic salts, such as sodium sulfate and potassium sulfate, present in a pulp slurry is small.

(Prior Art)

Although anionic polyacrylamides (polyacrylamide is referred to as "PAM," hereafter) have been used mostly in the past for individual use of a paper strengthening agent for the purpose of additional improvements in a closed white water owing to problems, such as drainage control, in shifting to neutral papermaking,, defective fixing of a sizing agent due

thereto, in water permeability, in the filler yield, etc. The method of use in systems where anionic PAMs and amphoteric (cationic) PAMs are combined has changed. By combining an anionic PAM with an amphoteric (cationic) PAM, the water-permeability, the fixing ability of the filler and sizing agent, the paper-strengthening effect, and the like were improved.

Most recently, a formula in which an anionic PAM and amphoteric (cationic) PAM are added simultaneously and a formulation in which they are added by mixing them have been developed, and additional water-permeability and sizing agent-fixing and paper-strengthening effects can be anticipated. However, two systems are required for anionic and amphoteric (cationic) use from the standpoint of equipment. It is known that the brightness highly regarded in the field of manufacturing paper in the Western manner also decreased significantly. The primary factors for this decrease in brightness in the paper was due to anywhere from cohesion of the anionic PAM and the amphoteric (cationic) PAM, to fine fibers, drainage system waste, and the like, which all reduce the brightness significantly. Furthermore, a decline in the paper texture may become a problem, depending on the degree of the cohesive power thereof.

Most recently, paper-strengthening agents manufactured by using acrylamides and cationic vinyl monomers of quaternary ammonium salts obtained by a reaction between a vinyl monomer comprising a tertiary amino group, vinyl monomers comprising an organic or inorganic acid salt of these or the tertiary amino group, and quaternizing agents, as the main raw materials, have begun to be used considerably. Although these paper-strengthening agents are generally used alone, they have a relatively

broad effective papermaking pH region in individual use. A reduction in the paper-strengthening degree, sizing agent-fixing effect, filler-yielding effect, a feature wherein the reduction in brightness is small, and so forth, are obtained. They presently cannot be as satisfactory in strength as a system in which an anionic PAM and amphoteric (cationic) PAM are combined.

(Problems to be Solved by the Invention)

The present invention provides a papermaking additive wherein the variation in the paper-strengthening effect is reduced with respect to a variation in the papermaking pH, and a variation in the paper-strengthening effect is small with respect to the dissolved constituents present in the pulp slurry.

(Means for Solving the Problems)

As a result of repeated painstaking investigations to solve these problems, the inventors of the present invention were led to completing the present invention, e.g., the following inventions:

1) A papermaking additive characterized by polymerizing a vinyl-based monomer composed essentially of a (meth)acrylamide monomer in the presence of a water-soluble polymer.

2) The composition of claim 1 wherein the water-soluble polymer is composed essentially of a reactive vinyl monomer and is a copolymer comprising one or more of the monomers (A) to (D) shown below.

(A) (Meth)acrylamide monomer

(B) Anionic vinyl monomer

(C) Cationic vinyl monomer

(D) Nonionic vinyl monomer

3) The composition of Claim (1) wherein the vinyl-based monomer polymerized in the presence of a water-soluble polymer is copolymerized with a homopolymer of a (meth)acrylamide, a (meth)acrylamide monomer, and further, a monomer selected from one or more monomers (E) to (G) shown below.

(E) Anionic vinyl monomer

(F) Cationic vinyl monomer

(G) Nonionic vinyl monomer

4) The composition of Claim (1) wherein the solid content, based on the water-soluble polymer, is 3 to 60 wt.% of the total solid content based on the final product obtained by polymerizing the vinyl-based monomer composed essentially of a (meth)acrylamide monomer in the presence thereof.

5) The composition of Claim 2 wherein the reactive vinyl monomer constituent is 0.01 to 20 mol.% in the water-soluble polymer. /609

6) A paper characterized by adding a range of 0.03 to 3 wt.% of the papermaking additive of Claim 1 with respect to the solid content of a pulp raw material for papermaking.

7) A method for manufacturing paper characterized by adding a range of 0.03 to 3 wt.% of the papermaking additive of Claim 1 with respect to the solid content of a pulp raw material for papermaking.

The present invention will be described in further detail.

Although it is a papermaking additive obtained by polymerizing a vinyl-based monomer composed essentially of a (meth)acrylamide monomer in the presence of a water-soluble polymer, the preferred constituent

units of this final product include: 50 to 97.9997 mol% of a (meth)acrylamide monomer constituent, 0.0003 to 12 mol% of a reactive vinyl monomer constituent, 0 to 20 mol% of an anionic vinyl monomer constituent, 2 to 50 mol% of a cationic vinyl monomer constituent, and 0 to 30 mol% of a nonionic vinyl monomer constituent. Consequently, these constituent units can be composed freely of the water-soluble polymer and the vinyl-based monomer polymerized in its presence.

Reasons that the amount of the reactive vinyl monomer constituent in the water-soluble polymer described in this patent is 0.01 to 20 mol% is because if the amount is less than 0.01 mol%, the paper-strengthening effect is reduced and if it is greater than 20 mol%, a moderate crosslinking reaction occurs between the water-soluble polymer itself and the vinyl-based monomer composed essentially of the (meth)acrylamide monomer in the presence of the water-soluble polymer, and the papermaking additive gels, resulting in being unusable.

The reactive vinyl monomer described in this patent is a monomer possessing a substituent having additional reactivity. N-alkoxymethyl(meth)acrylamide derivative, glycidyl(meth)acrylate, 3-chloro-2-hydroxypropyl(meth)acrylate, acryloein, and the like are cited as examples therefor. Including N-hydroxymethyl(meth)acrylamide, N-methylol(meth)acrylamide, N-methoxymethyl(meth)acrylamide, N-ethoxymethyl(meth)acrylamide, N-n-butoxymethyl(meth)acrylamide, N-tert-butoxymethyl(meth)acrylamide, and the like can be exemplified as examples of the N-alkoxymethyl(meth)acrylamide derivative.

Unsaturated carboxylic acids, such as maleic acid, fumaric acid, itaconic acid, acrylic acid, crotonic acid and citraconic acid, their alkaline metal salts, such as sodium or potassium salts, ammonium salts, or the like, of these, can be exemplified as examples of the anionic vinyl monomer. In addition, unsaturated sulfonic acids, such as vinyl sulfonic acid, allyl sulfonic acids, methacryl sulfonic acid, styrene sulfonic acid, 2-acrylamide-2-phenylpropanesulfonic acid and 2-acrylamide-2-methylpropane sulfonic acid, or alkaline metal salts, such as sodium or potassium salts, ammonium salts, and the like of these can be exemplified as examples.

The cationic vinyl monomer includes vinyl monomers having an amino group or organic or inorganic acid salts of these. (Meth)acrylic acid ester derivatives, such as dialkylaminoethyl(meth)acrylates and dialkylaminopropyl(meth)acrylates; (meth)acrylamide derivatives, such as dialkylaminoethyl(meth)acrylamide, dialkylaminopropyl(meth)acrylamide and (meth)acrylamide-3-methylbutyldimethylamine, can be exemplified as examples of the vinyl monomer having a tertiary amino group.

Quaternary ammonium salts obtained by a reaction between a vinyl monomer having a tertiary amino group and a quaternizing agent can be exemplified as the vinyl monomer having a quaternary ammonium salt, and an alkyl halide, dialkylsulfuric acid, epichlorohydrin, benzyl halide, and the like can be exemplified as the quaternizing agent. In addition, 2-hydroxy-3-methacryloyloxypropyltrimethyl ammonium chloride and diallyldimethyl ammonium chloride can be exemplified.

Unsaturated nitriles, such as acrylonitrile and methacrylonitrile; (meth)acrylic acid esters, such as methyl(meth)acrylate, butyl(meth)acrylate and hydroxyethyl(meth)acrylate; (meth)acrylamide /610 compounds, such as methoxymethyl(meth)acrylamide, butoxymethyl(meth)acrylamide and diacetone(meth)acrylamide; aromatic vinyl compounds, such as styrene and methyl styrene; and vinyl acetate; vinyl chloride; vinylidene chloride; N-vinylformamide; and the like can be exemplified.

The amount of the solid content based on the water-soluble polymer is 3 to 60 wt.% with respect to the total solid content, based on the final product obtained by polymerizing the vinyl-based monomer composed essentially of a (meth)acrylamide monomer in the presence thereof, although it is preferably 5 to 50 wt.%. The reason that this range is required is because if the amount is less than 3 wt.%, the problems to be solved by the present invention cannot be solved, and if it is greater than 60 wt.%, there are problems because the polymerization yield decreases and the danger of the compound gelling is extremely high.

A known method used in the polymerization of such a water-soluble vinyl monomer is used for the method for obtaining the copolymer of the present invention.

For example, a radical polymerization is preferred for the polymerization method. The monomer concentration is 2 to 30 wt.%, and preferably, 5 to 30 wt.%. As long as it is water-soluble, the polymerization initiator is not limited in particular; it can be used by dissolving it in an aqueous monomer solution normally. Specifically, peroxides, such

as hydrogen peroxide and benzoyl peroxide; persulfates, such as sodium persulfate, potassium persulfate and ammonium persulfate; perbromates, such as sodium perbromate and potassium perbromate; perborates, such as sodiumperborate, potassiumperborate and ammoniumperborate; percarbonates, such as sodium percarbonate, potassium percarbonate and ammonium percarbonate; perphosphates, such as sodium perphosphate, potassium perphosphate and ammonium perphosphate; tert-butylperoxide; and the like can be cited. In this case, the polymerization initiator can be used alone, but it can be used by combining it with a reducing agent or a redox polymerizing agent. Sulfites, hydrogen sulfites, lower ionized salts of iron, copper, cobalt, and the like; organic amines, such as N,N,N',N'-tetramethylethylenediamine, and further, reducing sugars, such as aldose and ketose; and the like can be cited as examples of the reducing agent.

In addition, 2,2'-azobis-4-amidinopropane hydrochloride, 2,2'-azobis-2,4-dimethylvaleronitrile, 4,4'-azobis-4-cyanopaleic acid, their salts, and the like may be used for the azo compound. Furthermore, two or more of the above-mentioned polymerization initiators can be combined.

The polymerization temperature is roughly 30 to 90°C lower than in the case of a single polymerization initiator and roughly 5 to 50°C lower than in the case of a redox polymerization initiator. In addition, it is not always necessary to keep the temperature the same during polymerization. As the polymerization proceeds, the temperature can be changed suitably. Generally the temperature is raised by the heat of the reaction generated as polymerization proceeds. The atmosphere in the reactor at that time

is not limited in particular, but in order to perform the polymerization rapidly, it is better to displace the reactor with an inert gas, such as nitrogen. The polymerization time is not limited in particular, but it is roughly 1 to 20 hours.

The molecular weight of the papermaking additive of the present invention is generally identical to papermaking additives used as PAM-based ones at the present, which can be a weight average molecular weight of about 100,000 to 2,000,000.

The papermaking additive of Claim 1 can be added to the solid content of a pulp raw material for papermaking in a range of 0.03 to 3 wt.%, but it is preferably 0.1 to 2 wt.%. The reason that this range is required is because if the solid content is less than 0.03 wt.%, the paper-strengthening effect is reduced and if it is greater than 3 wt.%, it is economically disadvantageous.

Any kind of pulp can be used while manufacturing paper according to the present invention. In addition, besides a papermaking additive used for a paper strengthening agent, as in the present invention, generally, an alumina polymer (aluminum sulfate, polyaluminum chloride, etc.), a sizing agent, filler, yield improver, and the like often can be added, but the present invention is not limited to these conditions.

(Effects)

According to the present invention, a papermaking additive could be provided for enhancing the paper-strengthening effect, and reducing the variation in the paper-strengthening effect, and further, the variation in the paper-strength effect with respect to a variation in

/611

the papermaking pH, and moreover, the variation in the paper-strengthening effect with respect to the dissolved constituents present in a pulp slurry.

The reasons thereof are not always clear, but it is surmised that, whereas a conventional PAM-based papermaking additive has a relatively straight chain structure, the PAM-based papermaking additive of the present invention has many structures including a partially branched or crosslinked one, or one in which the polymer envelopes the polymer. The paper has a structure where the pulp fibers having a diameter of from several microns to several tens of microns and a length of from several microns to several millimeters are entwined. In the improvement of the paper-strengthening effect of the PAM-based papermaking additive, it is said the hydrogen bonds are supplied between the pulp fibers. In order to replenish the hydrogen bonds between the pulp fibers of the paper having an extremely crude structure with the PAM-based papermaking additive, it is surmised that a 3-dimensional structure is more suitable than that of a conventional PAM-based papermaking additive. It is also surmised that this improvement is connected to improving the paper-strengthening effect of the PAM-based papermaking additive of this patent.

In addition, it is said that the electrical attractive force of the papermaking additive while fixing it to pulp acts centrally. Besides the effect of the PAM-based papermaking additive of this patent, in order to also physically fix it to the pulp, it is surmised that the aforementioned structure features, wherein the variation in the effect is small in terms of a variation in the papermaking pH, and moreover, the variation in the effect in terms of the dissolved constituents present in the pulp slurry

is small, are not provided.

(Practical Examples)

The present invention will now be described specifically by citing practical examples, but the present invention is not limited whatsoever by these practical examples.

Moreover, "%" and "part(s)" wholly represent wt.% and part(s) by weight unless otherwise noted.

Practical Example 1

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 180 parts methacryloyloxyethyltrimethyl ammonium chloride, 20 parts glycidyl methacrylate, used as the reactive vinyl monomer, and 750 parts water.

After that the internal temperature was raised to 30°C while blowing in nitrogen gas. A 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied under stirring to initiate polymerization and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by subsequently adding water, a water-soluble polymer (A) having a Brookfield viscosity of 12 poise at 25°C was obtained.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 150 parts of this water soluble polymer (A), 280 parts 40% acrylamide, 10 parts 80% acrylic acid and 400 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring,

a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, an aqueous solution having a Brookfield viscosity at 25°C of 57 poise was obtained.

Practical Example 2

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 225 parts 80% acrylic acid, 20 parts N-methylol acrylamide used as the reactive vinyl monomer, and 450 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution. The internal temperature was subsequently raised to 30°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, a water-soluble polymer (B) having a Brookfield viscosity at 25°C of 21 poise was obtained.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 80 parts of this water-soluble polymer (B), 235 parts 40% acrylamide, 40 parts dimethylaminoethylmethacrylate and 500 parts water. The pH was adjusted to 4.5 by adding a 20% aqueous sulfuric acid solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate

polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, an aqueous /612 solution having a Brookfield viscosity at 25°C of 50 poise was obtained.

Practical Example 3

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 385 parts 40% acrylamide, 5 parts dimethylaminopropylacrylamide, 20 parts 80% acrylic acid, 20 parts acrylonitrile, 5 parts N-methylol acrylamide used as the reactive vinyl monomer, and 500 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution. The internal temperature was subsequently raised to 30°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, a water-soluble polymer (C) having a Brookfield viscosity at 25°C of 11 poise was obtained.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 300 parts of this water-soluble polymer (C), 175 parts 40% acrylamide, 20 parts dimethylaminoethylmethacrylate and 400 parts water. The pH was adjusted to 4.5 by adding a 20% aqueous sulfuric acid solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the

total quantity to 1,000 parts by adding water thereafter, an aqueous solution having a Brookfield viscosity at 25°C of 61 poise was obtained.

Comparative Example 1

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 180 parts methacryloyloxyethyltrimethyl ammonium chloride and 750 parts water. The internal temperature was subsequently raised to 30°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, a water-soluble polymer (D) having a Brookfield viscosity at 25°C of 10 poise was obtained.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 150 parts of this water-soluble polymer (D), 280 parts 40% acrylamide, 10 parts 80% acrylic acid and 400 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, an aqueous solution having a Brookfield viscosity at 25°C of 51 poise was obtained. This is a comparative example when the reactive monomer according to Practical Example 1 is not used.

Comparative Example 2

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 225 parts 80% acrylic acid and 450 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution after that. The internal temperature was subsequently raised to 30°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, a water-soluble polymer (E) having a Brookfield viscosity at 25°C of 30 poise was obtained.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 80 parts of this water-soluble polymer (E), 235 parts 40% acrylamide, 40 parts dimethylaminoethyl methacrylate and 500 parts water. The pH was adjusted to 4.5 by adding a 20% aqueous sulfuric acid solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, an aqueous solution having a Brookfield viscosity at 25°C of 45 poise was obtained. This is a comparative example when the reactive monomer according to Practical Example 2 was not used.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 385 parts 40% acrylamide, 5 parts dimethylaminopropylacrylamide, 20 parts 80% acrylic acid, 20 parts acrylonitrile and 500 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution after that. The internal temperature was subsequently raised to 30°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, a water-soluble polymer (F) having a Brookfield viscosity at 25°C of 21 poise was obtained.

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 300 parts of this water-soluble polymer (F), 175 parts 40% acrylamide, 20 parts dimethylaminoethylmethacrylate and 400 parts water. The pH was adjusted to 4.5 by adding a 20% aqueous sulfuric acid solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, an aqueous solution having a Brookfield viscosity at 25°C of 58 poise was obtained. This is a comparative example when the reactive monomer according to Practical Example 3 was not used.

Comparative Example 4

A 4-necked flask provided with a stirrer, reflux condenser, thermometer and nitrogen gas introduction tube was charged with 27 parts methacryloyloxyethyltrimethyl ammonium chloride, 280 parts 40% acrylamide, 10 parts 80% acrylic acid and 400 parts water. The pH was adjusted to 4.5 by adding a 25% aqueous sodium hydroxide solution. The internal temperature was subsequently raised to 40°C while blowing in nitrogen air. Under stirring, a 10% aqueous ammonium persulfate solution and a 10% aqueous sodium hydrogen sulfite solution were supplied to initiate polymerization, and this was maintained for 3 hours. Upon bringing the total quantity to 1,000 parts by adding water thereafter, an aqueous solution having a Brookfield viscosity at 25°C of 54 poise was obtained. This is a comparative example when the water-soluble polymer using the reactive vinyl monomer according to Practical Example 1 was not present and the other vinyl monomer constituents except for the reactive vinyl monomer were polymerized all together to obtain the same composition as Practical Example 1.

Application Example 1

The pH was adjusted to standard 3 by adding aluminum sulfate to a 1% pulp slurry comprising old corrugated cardboard beat in 450 mL of CSF. The respective pHs of papermaking additives in which 0.5%, 1% and 2% aluminum sulfate were added to the pulp of a 1% pulp slurry were 6.5, 5.8 and 4.7. The papermaking additives manufactured in Practical Examples 1 to 3 and the papermaking additives manufactured in Comparative Examples 1 to 4 were added to these respective 1% pulp slurries so that the solid

content was 0.5% with respect to the pulp. Paper having a 150 g/m² weight basis was made from these pulp slurries using a Tappi standard sheet machine. The rupture strength was measured according to JIS P 8112 and the Z-axis strength was measured with an internal bonded tester made by Kumagai Riki Kogyo K.K. The results thereof are shown in Tables 1-1 and 1-2. Moreover, a blank indicates that no papermaking additive was added.

Application Example 2

The pH was adjusted to 5.5 by adding aluminum sulfate to a 1% pulp slurry of old corrugated cardboard beat with 450 mL CSF. Upon adding 0, 2,000, and 4,000 ppm sodium sulfate to this 1% pulp slurry, the electric conductivities of the respective 1% pulp slurries were 0.15, 2.70 and 5.21 mS/cm. The papermaking additives manufactured in Practical Examples 1 to 3 and the papermaking additives manufactured in Comparative Examples 1 to 4 were added to these respective 1% pulp slurries so that the solid content was 0.5% with respect to the pulp. These pulp slurries were made into paper having a 150 g/m² weight basis using a Tappi standard sheet machine. The rupture strength was measured according to JIS P 8112 and the compression strength was measured according to JIS P 8126. The results thereof are shown in Tables 2-1 and 2-2. Moreover, a blank indicates that no papermaking additive was added.

Application Example 3

The pH was adjusted to 5.5 by adding aluminum sulfate to a 1% pulp slurry of old corrugated cardboard beat with 430 mL of CSF. 0, 100, and 200 ppm sodium lignin sulfonate were added to this 1% pulp slurry. /614
The papermaking additives manufactured in Practical Examples 1 to 3 and

the papermaking additives manufactured in Comparative Examples 1 to 4 were added to these respective 1% pulp slurries so that the solid content was 0.5% with respect to the pulp. These 1% pulp slurries were made into paper having a 150 g/m² weight basis using a Tappi standard sheet machine.

The rupture strength was measured according to JISP 8112 and the compression strength was measured according to JIS P 8126. The results thereof are shown in Tables 3-1 and 3-2. Moreover, a blank indicates that no papermaking additive was added.

Table 1-1

Type of Papermaking Additive	Papermaking pH	Specific Rupture Strength	Z-Axis Strength (kg-cm)
Practical Example 1	4.7	2.36	2.21
Practical Example 1	5.6	2.41	2.25
Practical Example 1	6.5	2.39	2.24
Practical Example 2	4.7	2.39	2.18
Practical Example 2	5.6	2.43	2.20
Practical Example 2	6.5	2.45	2.29
Practical Example 3	4.7	2.45	2.25
Practical Example 3	5.6	2.49	2.25
Practical Example 3	6.5	2.46	2.31
Blank	4.7	1.81	1.46
Blank	5.6	1.84	1.46
Blank	6.5	1.85	1.51

Table 1-2

Type of Papermaking Additive	Papermaking pH	Specific Rupture Strength	Z-Axis Strength (kg-cm)
Comparative Example 1	4.7	2.23	2.02
Comparative Example 1	5.6	2.33	2.12
Comparative Example 1	6.5	2.35	2.26
Comparative Example 2	4.7	2.25	1.95
Comparative Example 2	5.6	2.31	2.13
Comparative Example 2	6.5	2.39	2.17
Comparative Example 3	4.7	2.16	1.97
Comparative Example 3	5.6	2.28	2.08
Comparative Example 3	6.5	2.36	2.19
Comparative Example 4	4.7	2.05	1.78
Comparative Example 4	5.6	2.22	1.91
Comparative Example 4	6.5	2.30	2.10

Table 2-1

Type of Papermaking Additive	Sodium Sulfate ppm	Specific Rupture Strength	Specific Compression Strength
Practical Example 1	0	3.66	18.7
Practical Example 1	2,000	3.61	18.6
Practical Example 1	4,000	3.59	18.6
Practical Example 2	0	3.65	18.6
Practical Example 2	2,000	3.66	18.4
Practical Example 2	4,000	3.61	18.3
Practical Example 3	0	3.72	18.8
Practical Example 3	2,000	3.64	18.8
Practical Example 3	4,000	3.60	18.5
Blank	0	2.83	16.6
Blank	2,000	2.81	16.4
Blank	4,000	2.82	16.6

Table 2-2

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Type of Papermaking Additive	Sodium Sulfate ppm	Specific Rupture Strength	Specific Compression Strength
Comparative Example 1	0	3.55	18.2
Comparative Example 1	2,000	3.46	18.0
Comparative Example 1	4,000	3.40	17.7
Comparative Example 2	0	3.55	18.0
Comparative Example 2	2,000	3.50	17.7
Comparative Example 2	4,000	3.43	17.4
Comparative Example 3	0	3.60	18.1
Comparative Example 3	2,000	3.53	18.0
Comparative Example 3	4,000	3.42	17.5
Comparative Example 4	0	3.45	17.8
Comparative Example 4	2,000	3.33	17.5
Comparative Example 4	4,000	3.20	17.0

Table 3-1

Type of Papermaking Additive	Sodium Lignin Sulfonate ppm	Specific Rupture Strength	Specific Compression Strength
Practical Example 1	0	2.59	16.5
Practical Example 1	100	2.60	16.5
Practical Example 1	200	2.54	16.3
Practical Example 2	0	2.57	16.3
Practical Example 2	100	2.55	16.4
Practical Example 2	200	2.51	16.0
Practical Example 3	0	2.63	16.7
Practical Example 3	100	2.57	16.5
Practical Example 3	200	2.56	16.5
Blank	0	1.89	14.4
Blank	100	1.87	14.6
Blank	200	1.90	14.5

Table 3-2

Type of Papermaking Additive	Sodium Lignin Sulfonate ppm	Specific Rupture Strength	Specific Compression Strength
Comparative Example 1	0	2.47	16.0
Comparative Example 1	100	2.35	15.7
Comparative Example 1	200	2.22	15.4
Comparative Example 2	0	2.49	15.9
Comparative Example 2	100	2.39	15.5
Comparative Example 2	200	2.25	15.4
Comparative Example 3	0	2.51	16.2
Comparative Example 3	100	2.44	15.9
Comparative Example 3	200	2.27	15.7
Comparative Example 4	0	2.37	15.8
Comparative Example 4	100	2.21	15.3
Comparative Example 4	200	2.02	15.0

(Advantages of the Invention)

According to the present invention, a paper-strengthening agent can be obtained that increases the paper-strengthening effect, and further, reduces the variation in the effect with respect to a variation in the papermaking pH, and moreover, the variation in the effect with respect to the dissolved constituents present in the pulp slurry.

That is, when the papermaking pH varies, as shown in Application Example 1, the paper-strengthening effects of the papermaking additives of Practical Examples 1 to 3 of the present invention are larger than the papermaking additives of Comparative Examples 1 to 4, which are not according to the present invention, while the variation in the paper-strengthening effect is smaller.

In addition, depending on the amount of sodium sulfate, which is a representative inorganic salt present in pulp slurries, as shown in Application Example 2, the paper-strengthening effect of the papermaking additives of Practical Examples 1 to 3 of the present invention are larger, than the papermaking additives of Comparative Examples 1 to 4, which are

not according to the present invention, while the variation in the paper-strengthening effect is smaller.

Furthermore, because the amount of sodium lignin sulfonate used as an example of organic matter in a pulp slurry changes, as shown in Application Example 3, the paper-strengthening effects of the papermaking additive of Practical Examples 1 to 3 of the present invention are larger than the papermaking additives of Comparative Examples 1 to 4, which are not according to the present invention, while the variation in the paper-strengthening effect is smaller. /616

The paper-strengthening effect of the papermaking additive of the present invention, as above, is high, and according to the variation in the papermaking pH and the variation in the amount of each type of dissolved constituent in a pulp slurry, it is evident that the papermaking additive is outstanding in resistance to the so-called variations in the papermaking conditions.